

# A STUDY TO EVALUATE OPTIMAL CATALYST PROPERTIES SOURCED FROM BIOWASTE FOR HYDRO PROCESSING OF USED COOKING OIL INTO GREEN DIESEL

**JOSIAH PELEMO, PROFESSOR FREDDIE INAMBAO, EMMANUEL I. ONUH  
& OMOJOLA AWOGBEMI**

*Mechanical Engineering Department, University of KwaZulu-Natal, Durban 4041, South Africa*

## ABSTRACT

*The need for alternative fuels to replace fossil-based fuels has been given more attention by various stakeholders. Commercial catalysts are a major component required for hydro processing of vegetable oil into hydrocarbon. However, the high cost of commercial catalysts hinders the commercialization of green diesel. This research work investigates the viability of biowaste fly ash collected from Eskom with supports like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO. These three support catalysts and BBTPPFS were pulverized, calcinated, and subjected to Brunauer-Emmett-Teller, thermal, spectroscopic, scanning electron microscope. A significant increase in the value of catalytic properties was noticed when 60 g BBTPPFS (sample D) was reinforced by adding 40 g of SiO<sub>2</sub> (Sample A) to obtain sample A1. The value of the micropore volume of -0.0001 cm<sup>3</sup> increased to 0.0014 cm<sup>3</sup>, and the surface area(external) increased from 0.8611 to 41.2571 m<sup>2</sup>/g, total surface area 0.5928 to 45.2771 m<sup>2</sup>/g and pore volume of 0.0053 increased to 0.1564 cm<sup>3</sup>/g. This combination showed properties that reveal it to be a potential green catalyst for hydrogenation and capable of mild cracking to achieve a green diesel range of C15-C18.*

**KEYWORDS:** HDRD, BBTPPFS, Heterogeneous Catalyst, Used Cooking Oil & Hydrogenation

**Received:** Jun 09, 2021; **Accepted:** Jun 29, 2021; **Published:** Aug 13, 2021; **Paper Id.:** IJMPERDOCT20213

## 1.0 INTRODUCTION

The sustained increase in demand for renewable energy across the globe has challenged researchers to develop and implement technologies for processing vegetable oils (edible and inedible) and animal fats into green diesel. The increase in energy demand can be traced to increased socioeconomic activities, industrialization, urbanization, modernization, and population growth [1]. The resulting increase in greenhouse gases (GHGs), and the depletion of fossil-based oil, has triggered the opinion for the search for alternative fuels that offer a pollution free environment and are sustainable. In recent years, the stakeholders have paid much attention to an effort to reduce the atmospheric temperature with policies to curb the effect, the members of legislative body otherwise known as the lawmakers have targeted pollution generated by automobile as major contributor to the GHGs which is one area to pay attention to. Despite the effort of the governments to offer a permanent solution to the threat posed by non-renewable energy and, depletion of oil reserves, the challenge is still on the increase and has attracted the attention of stakeholders globally.

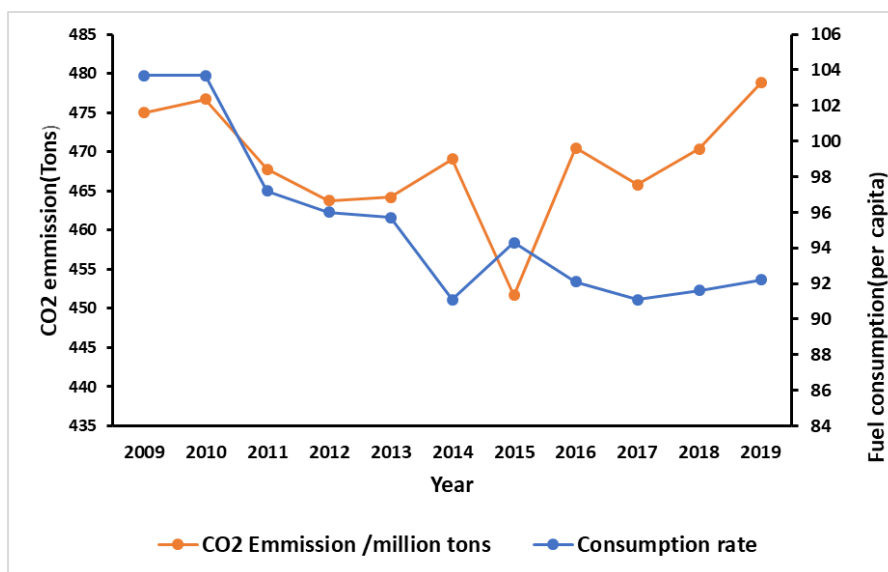
Hydrogenation-derived renewable diesel (HDRD), otherwise known as green diesel has emerged as the only feasible and sustainable automobile fuel. Hence, the pressing need for a transportation fuel that is suitable for a compression ignition engine without modifications. Therefore, more research is required by the scholars to

investigate the resource availability to produce HDRD that can will offer zero carbon to the environment. The tailpipe emissions generated by trucks and stationary engines are the major contributor to GHGs. Transportation sector is the second largest source to global warming [2]. About 92 million automobiles were produced globally in 2019 compared with about 56 million automobiles produced in 2001 [3]. Environmental Protection Agency (EPA), United States reported, carbon IV oxide ( $\text{CO}_2$ ) gases increased by 9 %, Methane emission decreased by 6% between 1990 and 2014. About 20 % of carbon dioxide discharged to the environment can be traced to daily activities such as transport-related emissions, which will continue to rise in the future [4].

Thermal power plants stations are set up to convert heat energy to electrical energy to meet the energy demands of society [5]. The waste generated from a power plant is usually referred to as coal ash, this is the end product of the burning of coals; the highest percentage is fly ash, while the coarse materials that settle at the base of the heating chamber are known as base or bottom ash. The fly ash product generated from burning any form of agricultural waste is known as Bio-Based Thermal Power Plant fly ash [6]. Elemental composition of bio-based ash is determined by the source of biomass and combustion technology. Therefore, BBTPFSs are different from coal ash in terms of their chemistry and mineralogy [7].

Several researchers have investigated and reported the adaptation of catalysts sourced from waste such as eggshell, mud shell, and soda-lime as being active catalysts for decarboxylation [8]. The motivation of the current research work is the addition of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  to BBTPFS to obtain a mixture that possesses optimal catalytic properties that can adequately mild crack used cooking oil (UCO) into the green diesel range. This study focuses on the evaluation of the optimal catalyst properties for hydrogenation. This research is set to determine the effect of calcinated support catalysts with freshly prepared BBTPFS heterogeneous catalysts, in order to characterize and evaluate the optimal properties for hydrogenation purposes. The scope of this study was to admixture a catalyst and its support, calcinate, and characterize the effect on the hydroprocessing of UCO.

Compression ignition (CI) engines in metro vehicles, stationary engines, agricultural machinery, etc. are the mainstay in power generation, transportation, and agriculture sectors. Carbon dioxide ( $\text{CO}_2$ ) comprises 74 % of GHG emissions, with about 89 % of  $\text{CO}_2$  emissions emanating from fossil fuel consumption in lighting, heating, transportation, and industrialization. Methane, nitrous oxide, and fluorinated gases make up 17.3 %, 6.2 %, and 2.1 % of total GHG emissions from agriculture, waste treatment, and industrial processes, respectively [9]. Figure 1 shows the consumption rate and  $\text{CO}_2$  emission in South Africa from 2009 to 2019. From this figure, it is evident that the consumption rate drops between 2015 to 2018 and rose in 2019, but there is a steady increment in the emission per million tons.



**Figure 1: Fuel Consumption (per capita) and CO2 Emission (tons) in South Africa from 2009 to 2019 [10].**

Catalytic hydro processing of vegetable oils for converting low-grade oils into HDRD has continued to attract more attention in recent years [11]. Utilization of biowaste catalysts for renewable diesel production has become more significant especially when it is generated or derived from waste materials [12]. The selection of a suitable catalyst offers good product with better properties; hence, selecting an appropriate catalyst for hydroprocessing purposes becomes a challenge. Hence, the need to critically study and evaluate the right catalyst that contains the properties suitable for the production of HDRD. The primary objective of catalyst activities in hydro-processing of a feedstock is to ensure adequate triglyceride conversion to a high quality and high yield of biofuel products by lowering the activation energy [13].

In South Africa, about 109 tons of coal is used per year by Eskom power stations, and about 25 million tons of ash is generated. However, 1.2 tons of coal fly ash are supplied to Lafarge for chemical additives in the cement industry. The bottom ash is a fine spherical particle, which has high pozzolanic activity (or reactivity), with unusually high consistency. Apart from the benefit of high quality and concrete economy fly ash also serve as a material for brick making and dam building. The construction of Katse Dam project received a supply of 250 000 tons of coal ash from Lethabo Power Station(LPS), In India, 90 metric tons of fly ash is generated per year and only 3% is used, while Germany used 80% of the coal fly ash product [14]. In most of the BBTPFS thermal power plant producing industries, the method of disposal adopted is either landfill without any restriction [8]. Waste generated and accumulated in an open space causes significant pollution in the environment that can impose health challenges in the geographical area. Indiscriminate disposal of waste products has a significant negative effect on underground water, then the land space occupied inhibits the use of large surface areas for other purposes. Solid waste produced by thermal power plants can be harnessed and used as a green catalyst that will significantly reduce the total cost of production of biofuel. As stated, BBTPFS is also usable by cement production companies [15, 16]. The volume of BBTPFS generation is increasing globally, which also increase the cost of waste management. In South Africa, this waste can be harness as potentials green catalyst resources [17]. The sulfur content in BBTPFS is lower, because is generated from biomass that has low sulfur content. In addition, this will further reduce GHGs effect caused by combustion of petroleum oil [18].

The properties and ionic composition of a catalyst greatly affect the hydro-processing of green diesel. Samples morphological of a catalyst was characterized using a transmission electron microscope (TEM) and a scanning electron microscope (SEM-EDS) from a single nanometric range to 500 nanometres. The structural dimension, molecular size, and the components of a catalyst provide enhance their activity during hydro processing. Brunauer-Emmett-Teller analysis provides information on surface area using a nitrogen adsorption/desorption analyser, while thermo-gravimetric analyser (TGA) examined the thermal stability of the catalysts.

Catalyst samples that have been applied in the production of biofuel as reported in the literature are nickel, columbium, and molybdenum. The active metals are mostly reinforced with aluminium oxide/silica dioxide [19]. Also, Columbium molybdenum, nickel catalysts and alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) are frequently used for hydro carboxylation, hydrodeoxygenation, and hydrogenation which are also good desulphurization catalysts [20]. Catalyst is to break the bonds and activate the route of C–C and C–O bond cleavage [21, 22]. However, any of the catalysts can be used for the activities, eg Ni-Mo/ $(\gamma\text{-Al}_2\text{O}_3)$  [22], Co-Mo [23], and CoMo/Si ( $\gamma\text{-Al}_2\text{O}_3$ ) [21]. The choice of hydro-processing route, reaction mechanism, and process parameter required will influence the selection of catalyst. [24]. Removal of oxygen from HDRD products during hydrogenation requires an appropriate selection of a catalyst to control the process of oxygen removal [25].

Varieties of commercial catalysts can be used for hydrogenation using vegetable oil or animal fats as a feedstock to obtain hydrocarbon products. The best route that offers optimal yield and high-quality biofuel product is hydro processing technology. Hydrodeoxygenation (HDO) and hydro isomerization routes are engaged to produce long-chain paraffins. The choice of route and catalyst suggests the yield and quality of HDRD. The objectives of this research work were to carry out a study to evaluate optimal catalyst properties for hydroprocessing of UCO with the aim of obtaining high quality green diesel. However, this poses the research question of which catalyst is suitable for conversion of UCO to HDRD, and how to identify the choice of catalyst/support structure that is capable of converting UCO into HDRD.

Musa balbisiana Colla underground stem (MBCUS), a nanomaterial, and a BBTPFS was used as a catalyst for hydro processing of *Jatropha curcas* oil and FFA *Mesua ferrea* L. and *Jatropha curcas* oil [26]. The conversion rate showed BBTPPTFS as the best catalyst that has the capacity to upgrade vegetable oil to an optimal yield than MBCUS. The catalyst potentials for upgrading vegetable oils to biofuel depend on the following properties among others: coking deactivation, resistance to water, and high deoxygenation activity [27]. These properties are found in BBTPPFS.

In this study, the catalysts underwent the following characterization: TGA, FTIR, SEM-EDS, TEM, x-ray diffraction (XRD), and BET. The outcome obtained from characterization suggested the type of catalyst with the best potential for catalytic hydroprocessing of UCO into green diesel. Catalytic parameters were investigated in order to identify the most suitable parameters to obtain an optimal yield

### 1.1 Bio-Based Thermal Fly Ash

Biomass is derived from plant material, the source of energy includes agricultural waste materials, wood waste, municipal solid waste, and methane captured from dumpsite. These waste materials can be harnessed and developed as catalysts which can be used effectively for the conversion of UCO to biofuel. This biowaste catalyst was found to be highly efficient for the hydro-processing of UCO to obtain 93.85 vol% and 66.29 vol.% of bio-crude and organic liquid fraction, respectively [28].

BBTPPFS has found applications in brick production, gas absorbents, glass and ceramics, and solid catalysts and catalyst reinforcements [29, 30]. The global ash market is projected to become USD 6.86 billion by the year 2026, up from USD 4.13 billion in 2018 [29]. Physically, BBTPPFS is lightweight ash, spherically shaped solid particles with sizes varying from 0.5  $\mu\text{m}$  to 300  $\mu\text{m}$ . The composition of a typical BBTPPFS is shown in Table 1 [31]. Waste ash is thrown in open ground or lagoons, causing mass environmental hazards and health risks. Eskom, a 100 % South Africa-owned enterprise, consumes an average of 120 million tons of coal per year generating 25 million tons of ash per year to produce 36 479 MW of electricity from its coal-fired stations [32] [33].

**Table 1: The Chemical Composition of BBTPPFS [34]**

Element	CaO	SiO <sub>2</sub>	MgO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Cl	Na <sub>2</sub> O
Composition (Wt%)	30.74	27.87	6.67	13.96	2.36	2.83	4.83	1.35	3.36	1.14

The following chemicals with insignificant percentage weight can also be found in bio-based thermal power plant ash, e.g., SrO, TiO<sub>2</sub>, MnO, ZrO<sub>2</sub>, BaO, ZnO, Br, Cr<sub>2</sub>O<sub>3</sub>, CuO, NiO, and As<sub>2</sub>O<sub>3</sub>. It is evident from Table 1 that the highest weight percentage is CaO and SiO<sub>2</sub>, with weight percentage 30.74 and 27.87, respectively. Both elements are the most active compounds for hydroprocessing catalysts [34].

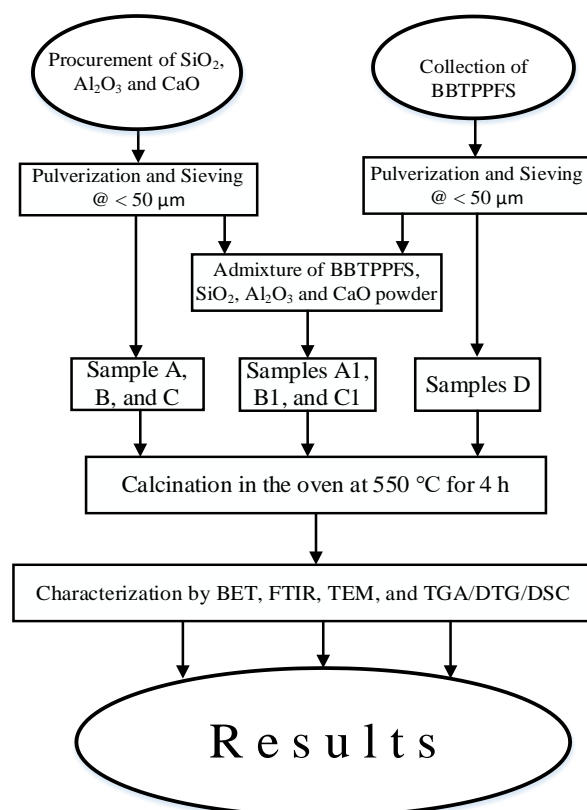
## 2.0 MATERIAL AND METHODS

### 2.1 Materials Collection and Sample Preparation

The BBTPPFS was sourced from Eskom from their Lethabo power generation plant, South Africa. Al<sub>2</sub>O<sub>3</sub>, CaO, and SiO<sub>2</sub> (analytical grade) were procured from Lichro Chemical and Laboratory Supplies, South Africa. The as-received catalyst was grinded into nano size using a mechanical grinder then sieved with a < 50  $\mu\text{m}$  mesh. The fine particle was dished into clean, dry, and airtight glass vials and labeled as indicated in Table 2. The BBTPPFS collected from ESKOM was ground into fine particles using an IKA MF 10 basic laboratory mechanical grinder and made to pass through sieve < 50  $\mu\text{m}$  mesh to ensure uniform particle size. The sieved BBTPPFS was measured, weighed, and transferred into a clean, dry, and airtight glass vial, and labeled as indicated in Table 2. The containers of the samples were kept in a cool environment to avoid contamination and oxidation. Figure 3 shows a flowchart of the preparation method of samples.

**Table 2: Details of Sample Preparation**

Sample Notation	Catalyst Samples			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	BBTPPFS
A	1	-	-	-
A1	1	-	-	1
B	-	1	-	-
B1	-	1	-	1
C	-	-	1	-
C1	-	-	1	1
D	-	-	-	1



**Figure 2: Flowchart of the Preparation Method of Samples.**

## 2.2 Catalyst

The samples were characterized using various techniques which includes SEM-EDX, XRD, FTIR, TGA, TEM, differential scanning calorimetry (DSC), and BET.

### 2.2.1 Thermal Analysis

The samples of seven calcinated dry powder fly ash, otherwise referred to as BBTPPFS, were subjected to thermal analysis using TGA (TA-60WS, Shimadzu) thermal analyzers. The aim was to observe the reaction of the samples at different temperature, which would aid the selectivity of the catalyst for hydrogenation. 10 mg of each sample was measured into an aluminium pan and scanned between 29 °C to 1000 °C, raising the heating rate 10 °C per minute, then held for 5 min at 1000 °C under nitrogen atmosphere at a flow rate of 10 ml/min in TGA and DSC analyser. The data were analysed using a TA-60 ch 1 DTG-60AH workstation.

### 2.2.2 Spectroscopic Analysis

This analysis is expected to offer a reliable absorption spectrum, the dilution and homogenization of the seven samples with spectroscopic grade. The experiment uses Perkin Elmer Co., USA, model 15.011, discs with 12.7 mm ID and  $\approx 1$  mm thick which was made of manual hydraulic press at about 10 tons for a time between 30 s to 60 s. The spectrum was measured from  $300\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  and recorded on a spectrometer of model system 1000 FTIR with a resolution of  $2.0\text{ cm}^{-1}$ . The applicability of BBTPPFS as a viable catalyst for conversion of UCO into HDRD depended on the location and peaks from the sample spectra.

### **2.2.3 BET Characterization**

Analysis of nitrogen sorption was carried out by a Micromeritics ASAP 2460 devices. 0.25 g of the seven samples were degassed at 100 °C under nitrogen gas for a night. Thereafter, the samples were kept in a vacuum to cool gradually to make their surfaces and pores available for close investigation. The surface area of the sample (m<sup>2</sup>/g) was computed by the BET method, while the pore size distributions, like the total pore volume (cm<sup>3</sup>/g at STP) and average pore radius (Å), were calculated using the Barrett-Joyner-Halenda (BJH) method. BET analyses revealed the pore volume, surface area, and pore area, which determined the capability of the sample as a potential green catalyst to mild crack UCO into green diesel.

### **2.2.4 TEM Analysis**

A Quorum Q150A ES sputtering machine was used as a platform to prepare the seven samples. The fly ash was analysed for morphology with the aid of Zeiss Ultra Plus in field emission gun scanning electron microscope (FEGSEM). However, A JEOL JEM-2100 operating at a speed of 20 kV was used for the high-resolution TEM analysis. The morphological, structural information unveiled through TEM analysis helped to determine catalysts that would support the hydrogenation of UCO.

### **2.2.5 XRD Analysis**

The fly ash powder was secured at the middle of sample holder and well positioned diffractometer D8-Advance manufactured by Bruker AXS(Germany). The measurement was observed in a continuous  $\theta$ - $\theta$  scan in locked coupled mode, tube; Cu-K $\alpha$  radiation ( $\lambda K\alpha_1=1.5406\text{\AA}$ ); detector; LynxEye (Position sensitive detector). The measurements ran within  $2\theta$  Range available from 0.5° to 130° in an Increment of  $\Delta 2\theta$ : (0.034°) at 0.5 sec/step. The phase analyses were done when the data were subtracted in line with diffraction pattern with zero background after choosing the identified elements from the periodic table. Phases were identified by comparing the calculated peaks with the measured ones until all phases had been identified within the limits of the resolution of the results. The results of the XRD analysis showed the elemental composition of the samples and their catalytic hydro-processing potentials.

### **2.2.6 SEM Analysis**

The SEM analysis was conducted on a Phenom ProX Desktop SEM. Desktop SEM with EDS has the capability of massive, easier, and flexible elemental and SEM analyses.

The samples were charged via an optional low vacuum sample holder with up to 25 mm diameter (optional 32 mm). SEM experiment was conducted at 15 kV in ambient temperature. The SEM outcome revealed sample images and the EDXS was used to determine the elemental composition which provided a structural idea of the biomass viability of the catalyst for hydrogenation of UCO.

## **3.0 RESULTS AND DISCUSSIONS**

### **3.1 Thermal Analysis**

The results of TGA of BBTPPFS collected from Eskom mixed with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO is shown in figure 3. The samples exhibited decomposition processes when subjected to heat in a controlled environment. It was observed that samples A1 and B1 followed the same pattern in response to thermal degradation. The weight loss occurred at 100 °C and 200 °C, respectively, and remained stable till to 1000 °C, which describes the thermal stability of the samples. This confirms that SiO<sub>2</sub> mixed with BBTPPFS catalyst had the ability to withstand the hydrogenation process to obtain a green

diesel product. Reports from literature indicate that calcination enhances decomposition of a catalyst [34, 35]. Therefore, the percentage weight loss (% weight loss) and the corresponding temperature obtained from Figure 3 shows that sample A, A1, B, B1, D maintained a thermal equilibrium considering the trend of decomposition. Sample A1 with 0.8 % weight loss at 99 °C with no additional loss in weight percentage reveals a potential catalyst for hydrogenation. This agrees with the calcination temperature of 550 °C adapted for this research. The thermal decomposition observed shows the sustainability of the catalyst in the face of the high temperature, up to 1000 °C. This could be traced to the high percentage of SiO<sub>2</sub> in the elemental composition of BBTPPFS as shown in Table 1. However, sample B has zero decomposition but could only be used as a supportive catalyst. Sample A's sharp decomposition may have been due to the moisture content and impurities contained in the sample but at 90 °C the sample slightly maintained a steady decomposition pattern up to 1000 °C and corresponding weight loss of 91 wt%. The reaction of sample D to the heat flow showed the ability of the sample to withstand heat which is a credit to its application for catalytic hydrogenation. The significant decomposition of calcium oxide occurred around 400 °C and 700 °C due to loss of water during the process and CO<sub>2</sub> from carbonated CaO. In contrast, C1 was a mixture of CaO and BBTPPFS; the decomposition pattern in Figure 3 was a result of high percentage of calcium oxide present in the fly ash. The addition of silica oxide (SiO<sub>2</sub>) support catalyst to heterogeneous (BBTPPFS) catalyst could improve the catalytic activity for hydroprocessing of green diesel. This result conforms with the findings as reported by Alipour et al. [36].

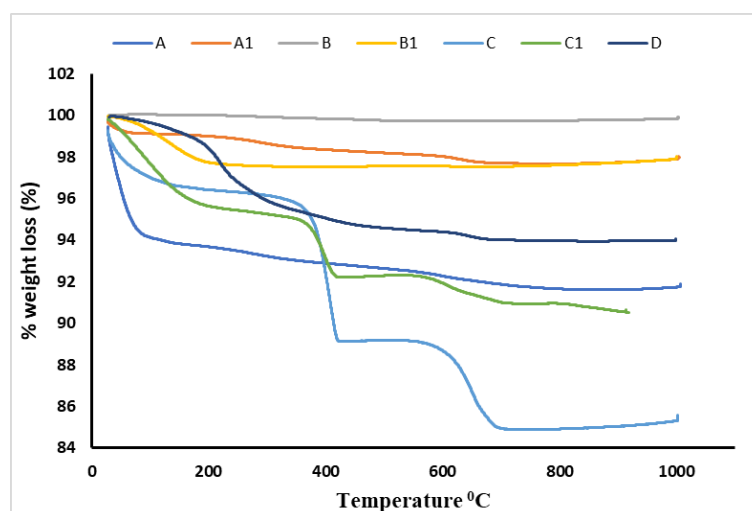
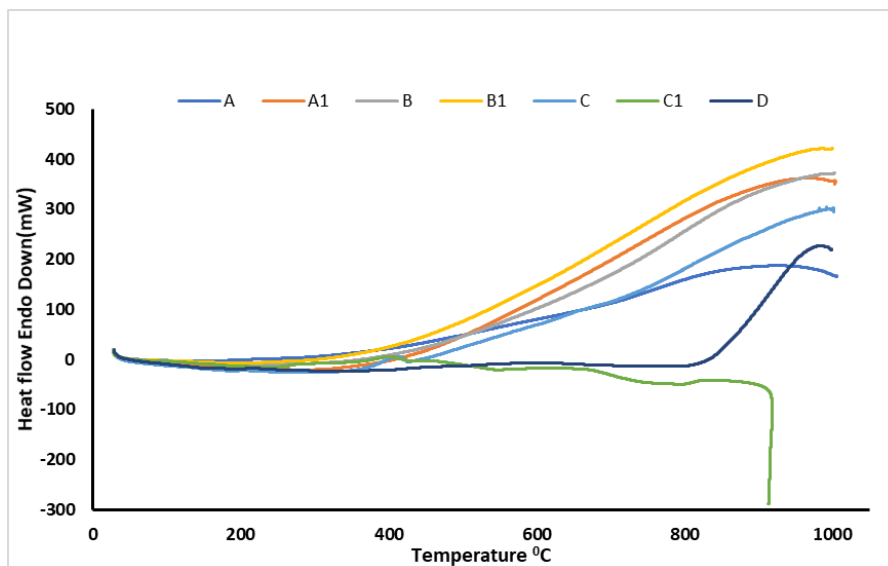


Figure 3: TGA Curve for the Samples.

### 3. 2 Differential Scanning Calorimetry(DSC)

The DSC curve reveals the endothermic reaction that occurred as a result of heat flow to the sample. Figure 4 shows the phase transformation in terms of thermal stability, the melting point of the heat reaction, and the crystallization point of the sample [37]. The heat flow follows the same pattern for samples A, A1, B, B1, C, D, while sample C1 behaved differently. From the curve, it is evident that the C1 sample could not absorb heat above 912 °C because of the moisture content and the presence of CO<sub>2</sub>. This implies that the samples possessed the ability to sustain heat at different phases during hydrogenation.





**Figure 4: DSC Curve for the Samples.**

### 3.3 Spectroscopic Analysis (FTIR)

Figure 5 is an FTIR spectra analysis that shows the wavelengths of samples with significant absorption bands. This effect can be traced to the addition of support catalyst samples to the BBTPPFS heterogeneous catalyst. This is in agreement with the findings of Maneerung et al. [38] and Sharma et al. [39]. Samples D, C1, and C values in the wavelengths with sharp absorption bands at  $3766\text{ cm}^{-1}$  and  $3613\text{ cm}^{-1}$  are noticed on the BBTPPFS, CaO, and BBTPPFS mixed with CaO catalyst, which is the -OH rhombohedral band. This band agrees with the presence of  $\text{CaCO}_3$  in samples D, C1, and C, but was not noticed in other samples, which is a confirmation of the result described by Boey et al. [40]. Samples A and A1 show a major absorption band at the wavelength of  $1084\text{ cm}^{-1}$  and  $707\text{ cm}^{-1}$ . This is attributed to the asymmetric O-Si-O while the wavelength at  $701\text{ cm}^{-1}$  in sample A has moved to  $707\text{ cm}^{-1}$  in sample A1. The peaks at  $707\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$  are due to the (Si, Al)-O-(Si, Al) symmetric stretching [28]. Also, the wide peak at  $2159\text{ cm}^{-1}$  was because of the (Si, Al)-O- (Si, Al) asymmetric transmission stretch. The absorption recorded by sample A1 falls within that reported by Arif et al. [41], who compared raw CFA with modified CFA. The outcomes of the FTIR analysis confirm the admixture of BBTPPFS and silica oxide as a potential catalyst for hydrogenation.

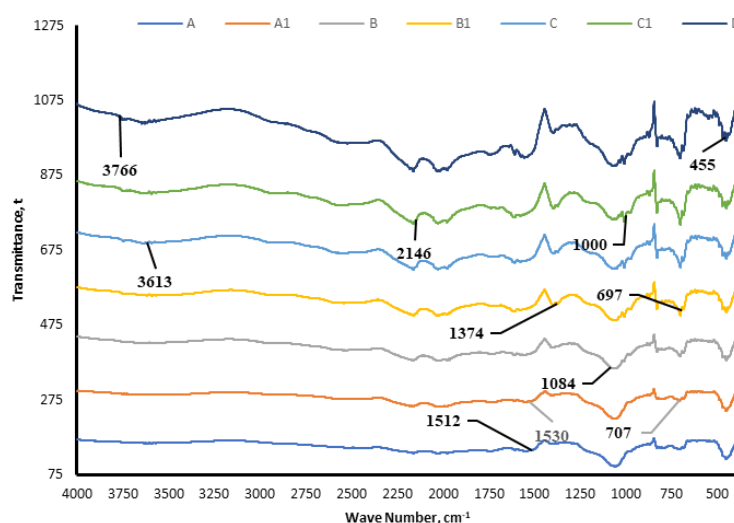


Figure 5: FTIR Spectra of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and BBTPPFS.

### 3.4 Brunauer-Emmett-Teller (BET) Analysis

Table 3: Textual Properties of the Samples

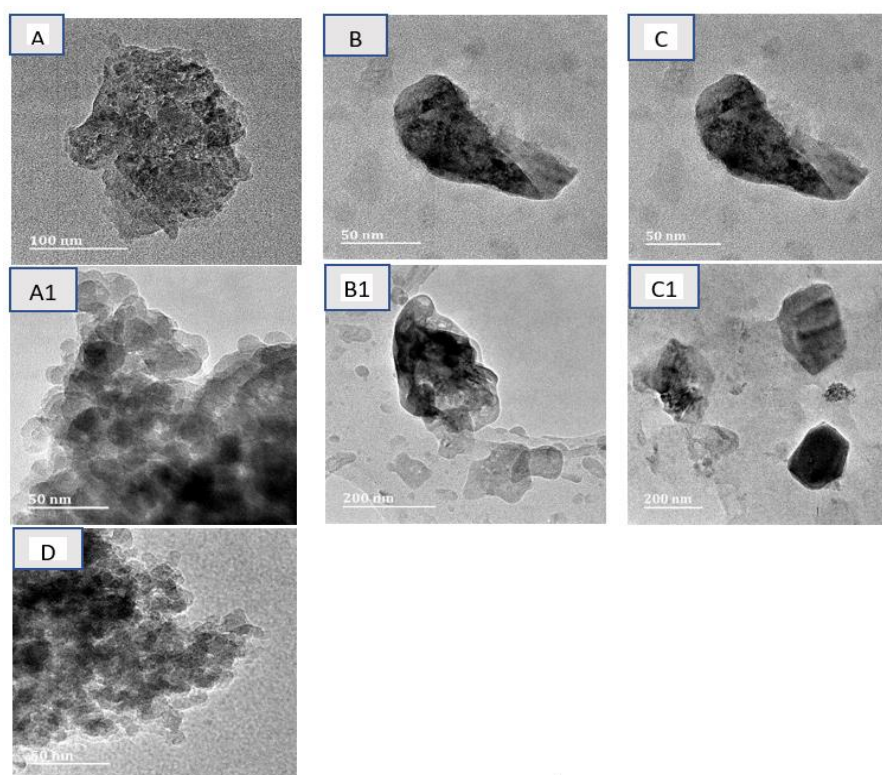
Properties	Samples							
	Unit	A	A1	B	B1	C	C1	D
Micropore Volume	cm <sup>3</sup> /g	0.0010	0.0014	-0.0002	-0.0003	0.0007	-0.0002	-0.0001
Micropore Area	m <sup>2</sup> /g	2.8080	4.0200	*NR	*NR	1.5244	*NR	*NR
External Surface Area	m <sup>2</sup> /g	30.6498	41.2571	0.4884	1.0087	2.9926	3.6274	0.8611
Total Surface Area	m <sup>2</sup> /g	33.4578	45.2771	0.0321	0.4581	4.5171	3.3098	0.5928
Pore Size	Å	141.3157	139.8311	*NR	245.0010	292.4526	204.1373	359.3611
Pore Volume	Cm <sup>3</sup> /g	0.1182	0.1564	0.0002	0.0029	0.03303	0.0169	0.0053
*NR- Not responding.								

The catalytic properties of BBTPPFS and support catalyst were investigated by BET. Table 3 shows the data analysis on the micropore volume, micropore area, external surface area, pore size, and pore volume. A significant increase was noticed when 60 g BBTPPFS (sample D) was modified by adding 40 g of SiO<sub>2</sub> (Sample A) to obtain sample A1. The values of micropore volume of -0.0001 cm<sup>3</sup> increased to 0.0014 cm<sup>3</sup>, and external surface area increased from 0.8611 to 41.2571 m<sup>2</sup>/g, total surface area from 0.5928 to 45.2771 m<sup>2</sup>/g, and pore volume of 0.0053 cm<sup>3</sup>/g increased to 0.1564 cm<sup>3</sup>/g. These values describe the ability of the green catalyst for HDRD optimal production. The parametric properties found in sample A1 support catalytic activities within the temperature range (300 °C to 400 °C) of mild cracking of the UCO for the purpose of hydrogenation to obtain green diesel in liquid hydrocarbon (C<sub>11</sub>-C<sub>18</sub>). This agrees with Deepak et al.'s findings [28]. The pore volume of 0.564 cm<sup>3</sup>/g in sample A1 falls within the range 0.08 cm<sup>3</sup>/g to 0.3 cm<sup>3</sup>/g reported when fly ash was synthesized, mixed with copper oxide, and converted to zeolites by hydrothermal activation, atmospheric crystallization, and double-stage fusion-hydrothermal for catalytic applications [42]. The value pore volume obtained in sample A1 is clear evidence that novel mesopores can be achieved by the admixture of two heterogeneous catalyst supports [41, 43]. The properties of a catalyst determine the choice of its selection; surface area as a physical property supports its catalytic activity. The higher the surface area the better the catalytic activity in terms of mild cracking and for more interactions with the reactants [25]. However, a high surface area of 45.2771 m<sup>2</sup>/g will speed up its catalytic activity for the adsorption and desorption of molecules such as triglycerides, glycerine, and green diesel [44, 45]. The outcome of the

BET analyses of samples reveals BBTPPFS mixed with SiO<sub>2</sub> as a potential green catalyst for the conversion of UCO into HDRD by hydrogenation [46, 47].

### 3. 5TEM Analysis

Heterogenous catalyst fly ash powder was examined using high-resolution transmission electron microscopy (HRTEM). Figure 6 shows the TEM micrographs with sample structural information. The calcined samples' mesostructure as detected in the TEM image is evidence of homogeneous active metals dispersed on the mesoporous structure [48]. The pore size and total surface area of BBTPPFS and its support enhance the catalytic activities capable of mild cracking the UCO during hydrogenation. Sample A1 has the highest pores and surface structure, and hexagonal-shaped particles compared to samples A, B, B1, C, C1, and sample D. This may due to the high weight percentage (wt.%) of calcinated SiO<sub>2</sub>. The TEM results is in line with XRD analysis. The calcinated sample (SiO<sub>2</sub> + BBTPPFS) A1 poses the properties that makes it viable for the conversion of UCO into HDRD using hydro processing technique as reported by Pandit and Fulekar [49] And Navajas et al. [50].



**Figure 6: TEM Micrograph for Sample (A, A1, B, B1, C, C1, and D).**

### 3.6 XRD Analysis

Table 4 describes the composition of major components of sample A, A1, B, B1, C, C1 and sample D. The percentage weight of calcinated sample D, BBTPPFS was 33.22 % quartz, 11.78 % mullite, 1.19 % calcite which increases to 100 % quartz, 41.67 % mullite, 2.08 % calcite respectively when sample A, SiO<sub>2</sub> was added. The significant increase is due to the predominant nature of silica oxide in BBTPPFS. Various studies available in the literature have proved that the existence of SiO<sub>2</sub> either as base or support catalyst increase the rate of hydrogenation of waste cooking oil [51, 52]. This characteristic points to sample A1, BBTPPFS<sub>ESKOM</sub> + SiO<sub>2</sub> with 100 % quartz as being a better green heterogeneous

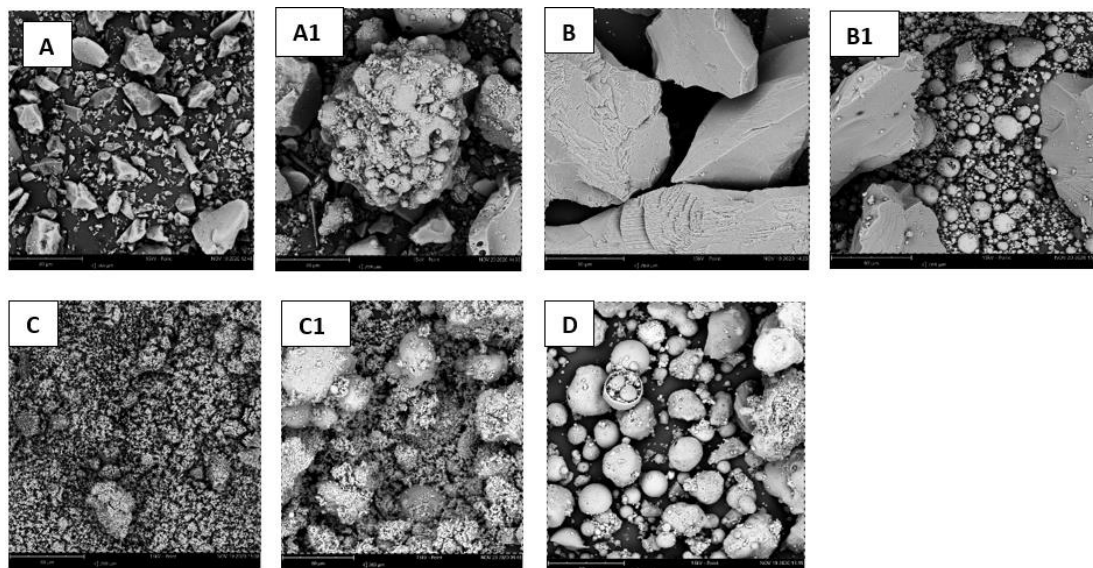
catalyst for hydro-processing of UCO to green diesel.

**Table 4: Composition of Major Components of the Samples**

Compound Name	Chemical Formula	Lattice	Sample Concentration %						
			A	A1	B	B1	C	C1	D
Quartz	SiO <sub>2</sub>	Hexagonal	-	100	-	20.83	-	12.15	33.22
Mullite	Al <sub>4</sub> Si	Hexagonal	-	41.67	-	4.17	-	4.17	11.78
Calcite	CaCO <sub>3</sub>	Rhombohedral	-	2.08	-	0.65	-	0.65	1.19
Corundum synthetic	Al <sub>2</sub> O <sub>3</sub>		-	-	100	8.33	76.15	42.13	-
Amonium Aluminium oxide.	(NH <sub>4</sub> ) <sub>2</sub> -Al-O		-	-	7.81	7.81	10.20	7.81	-

### 3.7 SEM Analysis

Scanning electron microscope (SEM) analysis was performed with the target to investigate surface morphology of a calcinated BBTPPFS heterogenous catalyst collected from Eskom with support catalysts added. The morphologies of the samples were very similar. Figure 7 shows a large and irregular particle of the samples. The image of BBTPPFS (sample D) indicates a spherical shape with a smooth surface. The image of sample A (SiO<sub>2</sub>) reinforced with sample D (BBTPPFS) reveals large surface and pores in sample A1, which was confirmed by XRD analysis. The weight percentage of gain and increase in silica oxide from 18.94 % to 25.65 % has a great impact in mild cracking of UCO to green diesel range. The white spots that appear on the catalyzed samples are elements from various categories. Silica oxide mixed with BBTPPFS has the tendency to withstand high temperatures up to 1000 °C, pointing to sample A1 being a reliable and superior green catalyst for hydrogenation.



**Figure 7: SEM Micrographs for Samples A, A1, B, B1, C, C1, and Sample D.**

## 4.0 CONCLUSIONS

Eskom generates a lot of fly ash from their power plants and discharges same in an environment which creates additional pollution in South Africa. This BBTPPFS waste can be harnessed as a green and biowaste catalyst to reduce the total cost of production of green diesel.

These research investigated the properties and effect of calcinated BBTPPFS, and three support catalysts were procured and used as received.

- BBTPPFS is available in tons in South Africa. Fly ash, which is a waste, can be harnessed to replace expensive commercial catalysts.
- The properties that favor catalytic hydrogenation were revealed by the results, which show that the surface area, external surface area, pore-volume, and micropore volume of calcinated BBTPPFS increased with the addition of SiO<sub>2</sub>. The effect of the reinforcement by the SiO<sub>2</sub> proves the novelty of the viable and potential catalyst for conversion of UCO to green diesel.
- The thermal decomposition observed shows that sample A1 (SiO<sub>2</sub> +BBTPPFS) catalyst could be sustained at a temperature up to 1000 °C. This temperature stability supports the hydroprocessing of UCO into HDRD.
- The percentage concentration of sample A1 increased from 33.22 % quartz to 100 % quartz, 11.78 % mullite to 41.67 % mullite, and 1.19 % calcite to 2.08 % calcite respectively. This increment was a result of the addition of SiO<sub>2</sub>.

The application of a calcinated 40 g silica oxide admixture with 60 g BBTPPFS increased the potential of a catalyst to mild crack UCO to green diesel.

### **Conflict of Interest**

There is no potential conflict of interest in this research work.

### **ACKNOWLEDGEMENT**

The authors are grateful to the leadership of Green Energy Solutions, Discipline of Mechanical Engineering, Howard College, University of KwaZulu-Natal, Durban for their contributions towards the success of this work.

### **REFERENCES**

1. British Petroleum. "BP statistical review of world energy June 2020," 2020. Available from <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2020-full-report.pdf>
2. N.-O. Nylund, P. Aakko-Saksa, and K. Sipilä, "Status and outlook for biofuels, other alternative fuels and new vehicles," 2008. Available from [http://www.globalbioenergy.org/uploads/media/0801\\_VTT\\_-\\_Status\\_and\\_outlook\\_for\\_biofuels\\_other\\_alternative\\_fuels\\_and\\_new\\_vehicles.pdf](http://www.globalbioenergy.org/uploads/media/0801_VTT_-_Status_and_outlook_for_biofuels_other_alternative_fuels_and_new_vehicles.pdf)
3. Statista. "Estimated worldwide automobile production from 2000 to 2019." Available from <https://www.statista.com/statistics/262747/worldwide-automobile-production-since-2000/>.
4. EPA, "Climate Change Indicators in the United States: U.S. Greenhouse Gas Emissions", [https://www.epa.gov/sites/production/files/2016-08/documents/print\\_us-ghg-emissions-2016.pdf](https://www.epa.gov/sites/production/files/2016-08/documents/print_us-ghg-emissions-2016.pdf)
5. H. Zhang, Z. Shen, and X. Liang, "The novel efficient catalyst for biodiesel synthesis from rapeseed oil," *Kinetics and Catalysis*, vol. 55, no. 3, pp. 293-298, 2014. <https://doi.org/10.1134/S002315841403015X>
6. A. Jaworek, T. Czech, A. T. Sobczyk, and A. Krupa, "Properties of biomass vs. coal fly ashes deposited in electrostatic precipitator," *Journal of Electrostatics*, vol. 71, no. 2, pp. 165-175, 2013. <https://doi.org/10.1016/j.elstat.2013.01.009>

7. R. Rajamma, R. J. Ball, L. A. Tarelho, G. C. Allen, J. A. Labrincha, and V. M. Ferreira, "Characterisation and use of biomass fly ash in cement-based materials," *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 1049-1060, 2009. <https://doi.org/10.1016/j.jhazmat.2009.07.109>
8. N. Carrara et al., "Selective hydrogenation by novel composite supported Pd egg-shell catalysts," *Catalysis Communications*, vol. 61, pp. 72-77, 2015. <https://doi.org/10.1016/j.catcom.2014.12.012>
9. Our World in Data. "Global greenhouse gas emissions". Available from <https://ourworldindata.org/greenhouse-gas-emissions>.
10. B. Looney, "Statistical review of world energy, 2020," ed: Bp, 2020.
11. A. P. S. Chouhan and A. K. Sarma, "Biodiesel production from *Jatropha curcas* L. oil using *Lemna perpusilla* Torrey ash as heterogeneous catalyst," *Biomass and Bioenergy*, vol. 55, pp. 386-389, 2013. <https://doi.org/10.1016/j.biombioe.2013.02.009>
12. W. W. S. Ho, H. K. Ng, and S. Gan, "Development and characterisation of novel heterogeneous palm oil mill boiler ash-based catalysts for biodiesel production," *Bioresource Technology*, vol. 125, pp. 158-164, 2012. <https://doi.org/10.1016/j.biortech.2012.08.099>
13. J. Xu et al., "Integrated catalytic conversion of waste triglycerides to liquid hydrocarbons for aviation biofuels," *Journal of Cleaner Production*, vol. 222, pp. 784-792, 2019. <https://doi.org/10.1016/j.jclepro.2019.03.094>
14. V. C. Pandey, P. Abhilash, and N. Singh, "The Indian perspective of utilizing fly ash in phytoremediation, phytomanagement and biomass production," *Journal of Environmental Management*, vol. 90, no. 10, pp. 2943-2958, 2009. <https://doi.org/10.1016/j.jenvman.2009.05.001>
15. S. Maschio, G. Tonello, L. Piani, and E. Furlani, "Fly and bottom ashes from biomass combustion as cement replacing components in mortars production: Rheological behaviour of the pastes and materials compression strength," *Chemosphere*, vol. 85, no. 4, pp. 666-671, 2011. <https://doi.org/10.1016/j.chemosphere.2011.06.070>
16. K. Trybalski, W. Kępyś, A. Krawczykowska, D. Krawczykowski, and D. Szponder, "Co-combustion of coal and biomass—chemical properties of ash," *Polish Journal of Environmental Studies*, vol. 23, no. 4, p. 1427, 2014.
17. J. Kalemkiewicz and U. Chmielarz, "Ashes from co-combustion of coal and biomass: New industrial wastes," *Resources, Conservation and Recycling*, vol. 69, pp. 109-121, 2012. <https://doi.org/10.1016/j.resconrec.2012.09.010>
18. E. Akbar, N. Binitha, Z. Yaakob, S. K. Kamarudin, and J. Salimon, "Preparation of Na doped SiO<sub>2</sub> solid catalysts by the sol-gel method for the production of biodiesel from *jatropha* oil," *Green Chemistry*, vol. 11, no. 11, pp. 1862-1866, 2009. <https://doi.org/10.1039/B916263C>
19. S. V. Vassilev, C. G. Vassileva, and V. S. Vassilev, "Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview," *Fuel*, vol. 158, pp. 330-350, 2015. <https://doi.org/10.1016/j.fuel.2015.05.050>
20. J. Chen and Q. Xu, "Hydrodeoxygenation of biodiesel-related fatty acid methyl esters to diesel-range alkanes over zeolite-supported ruthenium catalysts," *Catalysis Science & Technology*, vol. 6, no. 19, pp. 7239-7251, 2016. <https://doi.org/10.1039/C6CY01242F>
21. J.-S. Moon and Y.-K. Lee, "Support effects of Ni<sub>2</sub>P catalysts on the hydrodeoxygenation of guaiacol: in situ XAFS studies," *Topics in Catalysis*, vol. 58, no. 4-6, pp. 211-218, 2015. <https://doi.org/10.1007/s11244-015-0362-4>
22. Z. He, M. Hu, and X. Wang, "Highly effective hydrodeoxygenation of guaiacol on Pt/TiO<sub>2</sub>: Promoter effects," *Catalysis Today*, vol. 302, pp. 136-145, 2018. <https://doi.org/10.1016/j.cattod.2017.02.034>



23. M. Domínguez-Barroso, C. Herrera, M. Larrubia, and L. Alemany, "Diesel oil-like hydrocarbon production from vegetable oil in a single process over Pt–Ni/Al<sub>2</sub>O<sub>3</sub> and Pd/C combined catalysts," *Fuel Processing Technology*, vol. 148, pp. 110-116, 2016. <https://doi.org/10.1016/j.fuproc.2016.02.032>
24. R. Venter, T. Khethane, L. Radebe, K. Mashamaite, C. Schabert, and S. Marx, "Evaluation of cottonseed oil as co-feedstock for the hydroprocessing of petroleum middle distillates for diesel fuel production," *24th European Biomass Conference and Exhibition*, 2016. <https://doi.org/10.5071/24thEUBCE2016-3DO.3.2>
25. M. K. Poddar, S. Kumar, P. K. Das, M. R. Maurya, and A. K. Sinha, "hydroprocessing of aqueous phase of pyrolysis oil over NiMo/Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> in microchannel reactor," *Catalysis in Green Chemistry and Engineering*, vol. 2, no. 1, 2019. <https://doi.org/10.1615/CatalGreenChemEng.2019029780>
26. N. Arun, J. Maley, N. Chen, R. Sammynaiken, Y. Hu, and A. K. Dalai, "NiMo nitride supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for hydrodeoxygenation of oleic acid: Novel characterization and activity study," *Catalysis Today*, vol. 291, pp. 153-159, 2017. <https://doi.org/10.1016/j.cattod.2017.03.053>
27. S. Popov and S. Kumar, "Renewable fuels via catalytic hydrodeoxygenation of lipid-based feedstocks," *Biofuels*, vol. 4, no. 2, pp. 219-239, 2013. <https://doi.org/10.4155/bfs.12.89>
28. D. Singh, S. S. Sandhu, and A. K. Sarma, "An investigation of green diesel produced through hydro-processing of waste cooking oil using an admixture of two heterogeneous catalysts," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 40, no. 8, pp. 968-976, 2018. <https://doi.org/10.1080/15567036.2018.1468508>
29. R. A. Kruger, "Fly ash beneficiation in South Africa: creating new opportunities in the market-place," *Fuel*, vol. 76, no. 8, pp. 777-779, 1997. [https://doi.org/10.1016/S0016-2361\(96\)00190-1](https://doi.org/10.1016/S0016-2361(96)00190-1)
30. R. Blissett and N. Rowson, "A review of the multi-component utilisation of coal fly ash," *Fuel*, vol. 97, pp. 1-23, 2012. <https://doi.org/10.1016/j.fuel.2012.03.024>
31. M. Stanković, S. Pavlović, D. Marinković, M. Tišma, M. Gabrovska, and D. Nikolova, "Solid green biodiesel catalysts derived from coal fly ash," *Renewable Energy–Resources, Challenges and Applications*, IntechOpen, London, pp. 185-208, 2020. <https://doi.org/10.5772/intechopen.91703>
32. Eskom. [https://www.eskom.co.za/OurCompany/CompanyInformation/Pages/Company\\_Information.aspx](https://www.eskom.co.za/OurCompany/CompanyInformation/Pages/Company_Information.aspx).
33. A. Eberhard, "The future of South African coal: Market, investment and policy challenges," Working paper 100, Stanford program on Energy and Sustainable Development, Freeman Spogli Institute for International Studies: Stanford University, Stanford, CA., USA. 2011.
34. P. Kumar et al., "Characterization, activity and process optimization with a biomass-based thermal power plant's fly ash as a potential catalyst for biodiesel production," *RSC Advances*, vol. 5, no. 13, pp. 9946-9954, 2015. <https://doi.org/10.1039/C4RA13475C>
35. S. A. Salaudeen, S. H. Tasnim, M. Heidari, B. Acharya, and A. Dutta, "Eggshell as a potential CO<sub>2</sub> sorbent in the calcium looping gasification of biomass," *Waste Management*, vol. 80, pp. 274-284, 2018. <https://doi.org/10.1016/j.wasman.2018.09.027>
36. Z. Alipour, M. Rezaei, and F. Meshkani, "Effects of support modifiers on the catalytic performance of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in CO<sub>2</sub> reforming of methane," *Fuel*, vol. 129, pp. 197-203, 2014. <https://doi.org/10.1016/j.fuel.2014.03.045>
37. L. Panda and S. Dash, "Characterization and utilization of coal fly ash: a review," *Emerging Materials Research*, vol. 9, no. 3, pp. 921-934, 2020. <https://doi.org/10.1680/jemmr.18.00097>

38. T. Maneerung, S. Kawi, and C.-H. Wang, "Biomass gasification bottom ash as a source of CaO catalyst for biodiesel production via transesterification of palm oil," *Energy Conversion and Management*, vol. 92, pp. 234-243, 2015. <https://doi.org/10.1016/j.enconman.2014.12.057>
39. M. Sharma, A. A. Khan, S. Puri, and D. Tuli, "Wood ash as a potential heterogeneous catalyst for biodiesel synthesis," *Biomass and Bioenergy*, vol. 41, pp. 94-106, 2012. <https://doi.org/10.1016/j.biombioe.2012.02.017>
40. P.-L. Boey, S. Ganesan, S.-X. Lim, S.-L. Lim, G. P. Maniam, and M. Khairuddean, "Utilization of BA (boiler ash) as catalyst for transesterification of palm olein," *Energy*, vol. 36, no. 10, pp. 5791-5796, 2011. <https://doi.org/10.1016/j.energy.2011.09.005>
41. A. Hidayat, A. Chafidz, and B. Sutrisno, "Utilization of Modified Coal Fly Ash (CFA) as a Catalyst for Production of Biodiesel from Coconut Oil: Part 1-Characteristics of the Catalyst," in *Materials Science Forum*, 2020, vol. 981, pp. 190-195: Trans Tech Publ. <https://doi.org/10.4028/www.scientific.net/MSF.981.190>
42. S. Boycheva et al., "Progress in the utilization of coal fly ash by conversion to zeolites with green energy applications," *Materials*, vol. 13, no. 9, p. 2014, 2020. <https://doi.org/10.3390/ma13092014>
43. O. Awogbemi, F. Inambao, and E. I. Onuh, "Modification and characterization of chicken eggshell for possible catalytic applications," *Heliyon*, vol. 6, no. 10, p. e05283, 2020. <https://doi.org/10.1016/j.heliyon.2020.e05283>
44. E. M. Vargas, L. Ospina, M. C. Neves, L. A. Tarelho, and M. I. Nunes, "Optimization of FAME production from blends of waste cooking oil and refined palm oil using biomass fly ash as a catalyst," *Renewable Energy*, vol. 163, pp. 1637-1647, 2021. <https://doi.org/10.1016/j.renene.2020.10.030>
45. M. Thommes et al., "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)," *Pure and Applied Chemistry*, vol. 87, no. 9-10, pp. 1051-1069, 2015. <https://doi.org/https://doi.org/10.1515/pac-2014-1117>
46. M. R. Khodadadi, I. Malpartida, C.-W. Tsang, C. S. K. Lin, and C. Len, "Recent advances on the catalytic conversion of waste cooking oil," *Molecular Catalysis*, vol. 494, p. 111128, 2020. <https://doi.org/10.1016/j.mcat.2020.111128>
47. I. Nikolopoulos, G. Kogkos, E. Kordouli, K. Bourikas, C. Kordulis, and A. Lycourghiotis, "Waste cooking oil transformation into third generation green diesel catalyzed by nickel–alumina catalysts," *Molecular Catalysis*, vol. 482, p. 110697, 2020. <https://doi.org/10.1016/j.mcat.2019.110697>
48. A. A. Ayodeji, O. E. Modupe, B. Rasheed, and J. M. Ayodele, "Data on CaO and eggshell catalysts used for biodiesel production," *Data in Brief*, vol. 19, pp. 1466-1473, 2018. <https://doi.org/10.1016/j.dib.2018.06.028>
49. P. R. Pandit and M. Fulekar, "Egg shell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology," *Journal of Environmental Management*, vol. 198, pp. 319-329, 2017. <https://doi.org/10.1016/j.jenvman.2017.04.100>
50. A. Navajas, T. Issariyakul, G. Arzamendi, L. Gandía, and A. Dalai, "Development of eggshell derived catalyst for transesterification of used cooking oil for biodiesel production," *Asia-Pacific Journal of Chemical Engineering*, vol. 8, no. 5, pp. 742-748, 2013. <https://doi.org/10.1002/apj.1715>
51. Y. Zhao et al., "Hydrogenation of diesters on copper catalyst anchored on ordered hierarchical porous silica: Pore size effect," *Journal of Catalysis*, vol. 357, pp. 223-237, 2018. <https://doi.org/10.1016/j.jcat.2017.11.006>



52. E. Lam, K. Larmier, P. Wolf, S. Tada, O. V. Safonova, and C. Copéret, "Isolated Zr surface sites on silica promote hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH in supported Cu catalysts," *Journal of the American Chemical Society*, vol. 140, no. 33, pp. 10530-10535, 2018. <https://doi.org/10.1021/jacs.8b05595>
53. Girish, C. R. "Catalyst preparation from various naturally available waste Materials for biodiesel production: a review." *International Journal of Mechanical and Production Engineering Research and Development* 9.6: 117-130.
54. Bhaskar, K., et al. "Effect of dimethoxy-methane (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>) additive on emission characteristics of a diesel engine fueled with biodiesel." *International Journal of Mechanical and Production Engineering Research and Development* 8.1: 399-406.
55. Al-Sharidi, Saleh H., Husin Sitepu, and Noktan M. AlYami. "Application of tungsten oxide (WO<sub>3</sub>) catalysts loaded with Ru and Pt metals to remove MTBE from contaminated water: A case of laboratory-based study." *IMPACT: International Journal of Research in Engineering & Technology*,: 19-30.
56. Krishna, V. Murali. "Heat Transfer Enhancement by using CuO-Water Nanofluid in a Concentric Tube Heat Exchanger-an Experimental Study." *International Journal of Mechanical Engineering (IJME)* 6.1: 11-20.

